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EFFICIENT HIGH-ENERGY HC1 CHEMICAL LASER

Leonard Y. Nelson, et al

Mathematical Sciences Northwest, Incorporated

MATHEMATICAL SCIENCES NORTHWEST, INC.
P.O. BOX 1887   BELLEVUE, WASHINGTON 98009

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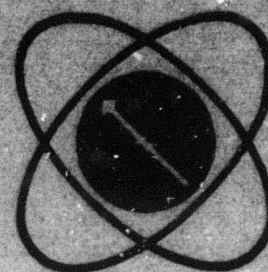
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Vibrational excitation of H_2 by an electron beam stabilized discharge is being investigated as a means of improving the performance of the HCl chemical laser. Recent calculations have shown that a nearly thousand fold increase in the rate limiting $Cl + H_2$ chain reaction step can be achieved by exciting H_2. Preliminary experiments indicate substantial laser output enhancement via a stabilized discharge excitation. Diagnostics for measuring $HCl(v)$, $H_2(v)$ and Cl_2 are being assembled.

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EFFICIENT HIGH-ENERGY HC1 CHEMICAL LASER

by

Leonard Y. Nelson
and
Stanley R.Byron

Mathematical Sciences Northwest, Inc.
P. O. Box 1887
Bellevue, Washington 98009

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                              (206) 827-0460

SCIENTIFIC OFFICER: Director, Physics Programs
                              Physical Sciences Division
                              Office of Naval Research
                              800 North Quincy Street
                              Arlington, Virginia 22217
                              Attn: Robert E. Behringer, Code 421

SHORT TITLE OF WORK: Efficient High-Energy HCl Chemical Laser

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SECTION I

SUMMARY

During the course of the present contract period, an experimental and analytical program has been initiated to investigate the improved performance of an HCl chemical laser using vibrationally excited H_2 to increase the rate of the slow chain reaction step ($Cl + H_2$). Preliminary experiments in a plasma diode electron-beam-stabilized electric discharge facility indicated that a substantial enhancement of the HCl laser emission was obtained when a low E/N voltage was applied across the laser gas mixture. The observed laser emission was a factor of 10 greater than the laser emission obtained with the electron beam alone. A further increase by a factor of 10 was obtained by adding a short duration high E/N discharge. The maximum output energy obtained was 20 millijoules corresponding to 0.2 j/ℓ-atm. Further tests are currently in progress using a much higher current (cold cathode) electron beam source, where substantially higher laser output can be expected. Parametric laser performance in this new device will be mapped out during the remainder of the present contract.

Recently, Wilkins (Ref. 1) has completed trajectory calculations of the rates of the chemical reactions involved in the HCl chemical laser. His work clearly shows three orders of magnitude increase in the rate of the cold reaction for $H_2(v = 1)$ compared with $H_2(v = 0)$. At the same time, Wilkins' (Ref. 2) fast V-T decay rate for HCl(v) due to Cl atoms is within a factor of 2 of that found experimentally by Macdonald and Moore

(Ref. 3). This new rate information indicates that it is essential to make use of vibrationally excited H_2 in order to reach interesting energy densities and efficiencies for the HCl chemical laser. These, and other rate data, together with all of the electron impact excitation cross sections for H_2/Cl_2/diluent mixtures, are being collected at MSNW for use in a comprehensive computer model of the electrically excited HCl chemical laser.

Diagnostics for measuring the molecular Cl_2 concentration, HCl(v) populations, and the extent of H_2 vibrational excitation produced by the discharge and its effect on the cold reaction rate were also being developed during the present contract period. Equipment for the Coherent Raman Anti-Stokes Scattering technique for measuring H_2(v) populations was ordered, and preliminary experiments using benzene are planned. Following successful completion of Raman experiments in liquid benzene, where the dye laser linewidth can be ten times larger than for hydrogen, the dye laser linewidth will be narrowed for the hydrogen experiments. Line narrowing by use of a dual etalon scheme, as required for a coherent Raman measurement in hydrogen is being evaluated.

SECTION II

HC1 LASER EXPERIMENTS

2.1. Laser Measurements in the Plasma Diode Electron Gun

Using the plasma diode electron gun facility at MSNW (Ref. 4) laser experiments were conducted in $Ar/H_2/Cl_2$ mixtures. Chlorine (Matheson, Research Grade), hydrogen (Airco, Grade 5), and argon (Airco prepurified) were all used directly without further purification. After each discharge pulse the discharge chamber was evacuated down to 1 torr and then refilled for the next run. The gas mixtures were made by mixing the gases in 1/8-in. I.D. polyethylene and copper tubing upstream of the discharge chamber.

Laser measurements were made in a high-Q cavity using CaF_2 Brewster angle windows on the discharge chamber and two 2 meter radius of curvature gold coated cavity mirrors spaced approximately 1.5 meters apart. A tilted CaF_2 flat was inserted into the cavity as a variable output coupler (Ref. 4). A "rat's nest" energy meter, with a sensitivity of 0.6 J/millivolt, was used to measure the energy reflected out of the cavity by the tilted CaF_2 flat. A liquid nitrogen cooled Ge:Au detector monitored the laser cavity intensity by viewing the small fraction of radiation scattered by the Brewster angle windows.

The discharge circuitry was slightly modified to allow a small, short pulse, high voltage secondary sustainer discharge capacitor to be used in conjunction with the larger, longer pulse duration, lower

voltage primary sustainer capacitor. The smaller capacitor could be fired at any time delay with respect to the principal discharge pulse or it could be fired alone.

Table I summarizes the results of laser experiments with the dual sustainer arrangement. It was observed that the cavity intensity increased by more than an order of magnitude when the low voltage sustainer was used compared to the electron beam alone. The laser energy increased by an order of magnitude when the high voltage sustainer was fired in addition to the low voltage sustainer. Also shown in Table I are estimates for the H atom and $H_2(v)$ concentrations, based on solutions to the Boltzmann equation for a 50/50 Ar/H_2 mixture in the absence of Cl_2. (See Ref. 4 for details of the method.) The estimates for the chlorine atom concentration given in Table I were obtained from the measured electron beam current density, and the assumption that every ionization yielded 2 Cl atoms.

Figure 1 presents oscillograms of the HCl laser emission under the conditions given in Table I. The low discharge currents are a result of the large electron attachment rate for Cl_2. These losses limit the maximum chlorine fraction to about 1 percent.

The higher HCl laser output obtained with the large, low voltage sustainer can be related to the production of $H_2(v)$ and an accelerated cold reaction rate. The addition of the short, high voltage sustainer leads to increased Cl_2 and H_2 dissociation, as well as $H_2(v)$ production. It is extremely difficult at this point to make a quantitative

TABLE I

PERFORMANCE OF AN ELECTRICALLY INITIATED
HCl CHEMICAL LASER SYSTEM

| | | INITIATION METHOD | |
	E-Beam	E-Beam Plus Low Voltage Discharge	E-Beam Plus High Voltage Discharge
Energy Input (J/ℓ-atm)	2	30	50 (upper limit)
Laser Energy (J/ℓ-atm)	< 0.01	0.02	0.2
Chemical Efficiency	< 1.2×10^{-4}	2.5×10^{-4}	2.5×10^{-3}
Discharge E/N (10^{-16}V-cm^2)		1.9	6 (upper limit)
$[H_2(v)]/[H_2]$		0.02	0.01
$[H]/[H_2]$		2×10^{-5}	4.5×10^{-3}
$[Cl]/[Cl_2]$	3×10^{-3}		

Gas mixture: Ar/H_2/Cl_2 (49.5/49.5/1)

Pressure: 200 torr
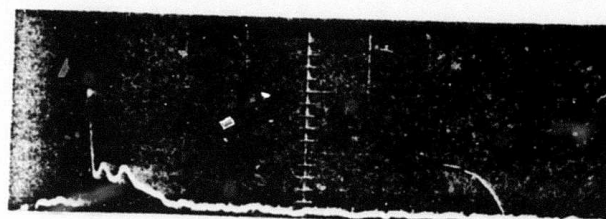
a) e-beam only

↑ IR Detector

⊢ 10 μsec/cm
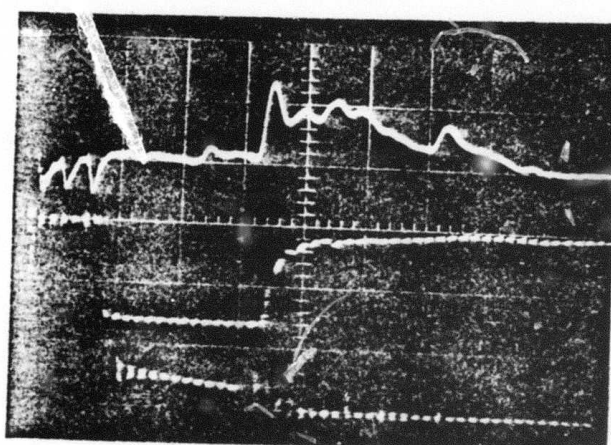
b) Low Voltage Electric Discharge

↑ IR Detector

↓ Discharge Voltage 800 V/cm/Div

↑ Discharge Current 274 V/cm/Div

⊢ 5 μsec/cm
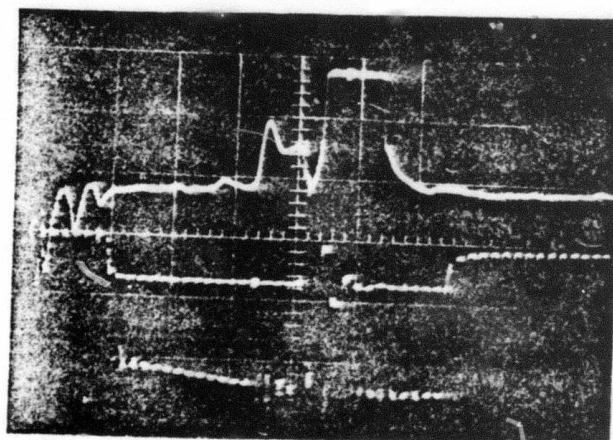
c) Low Voltage + High Voltage Electric Discharges

IR Detector [Flat Peak due to Saturation]

Discharge Voltage 1600 $\frac{V/cm}{Div}$

Discharge Current 274 A/Div

Figure 1. HCl Laser Emission Observed in the Plasma Diode Electron Gun Facility. Ar/H_2/Cl_2 (49.5/49.5/1). P_{total} = 200 torr.

evaluation of the effect of the sustainer banks without diagnostic tools to measure the important chemical species and reactions. The development of these diagnostic methods is described in Section 2.3.

2.2. Increased Electrical Excitation Capability

In order to permit the use of higher Cl_2 concentrations and to achieve an increased hydrogen vibrational excitation rate, a higher current electron beam source has been developed. The electron gun is shown schematically in Figure 2 and typical performance characteristics are shown in Figure 3. The cold cathode design (John Rink, LASL) incorporates an electric field configuration capable of providing stable e-beam operation for pulse durations of 10 μsec at an average current density of 0.2 - 0.3 amps/cm² and for 5 μsec at 0.7 - 0.8 amps/cm². The long pulse duration has been achieved in this device by utilizing electrostatic focussing at the torus shaped cathode to confine the current to the central portion of the electrodes and by maintaining a very low background gas pressure and eliminating small pinhole leaks. The gun foil transmission area is 10 cm by 50 cm. Operation at 180 kV has been achieved without the need for crowbarring the gun voltage.

Testing of this new electron gun facility has been completed, and it is currently being prepared for use in the HCl laser program.

2.3. Diagnostics and Kinetic Measurements

In order to obtain a quantitative understanding of the laser performance, it is essential to measure the production of $H_2(v)$ in the discharge and its removal by Cl atoms, as well as the HCl(v) production and deactivation rate. The chlorine, $H_2(v)$ and HCl(v) concentrations will be measured using the diagnostic methods described below.

Figure 2. Cross-Sectional View of Cold Cathode Electron
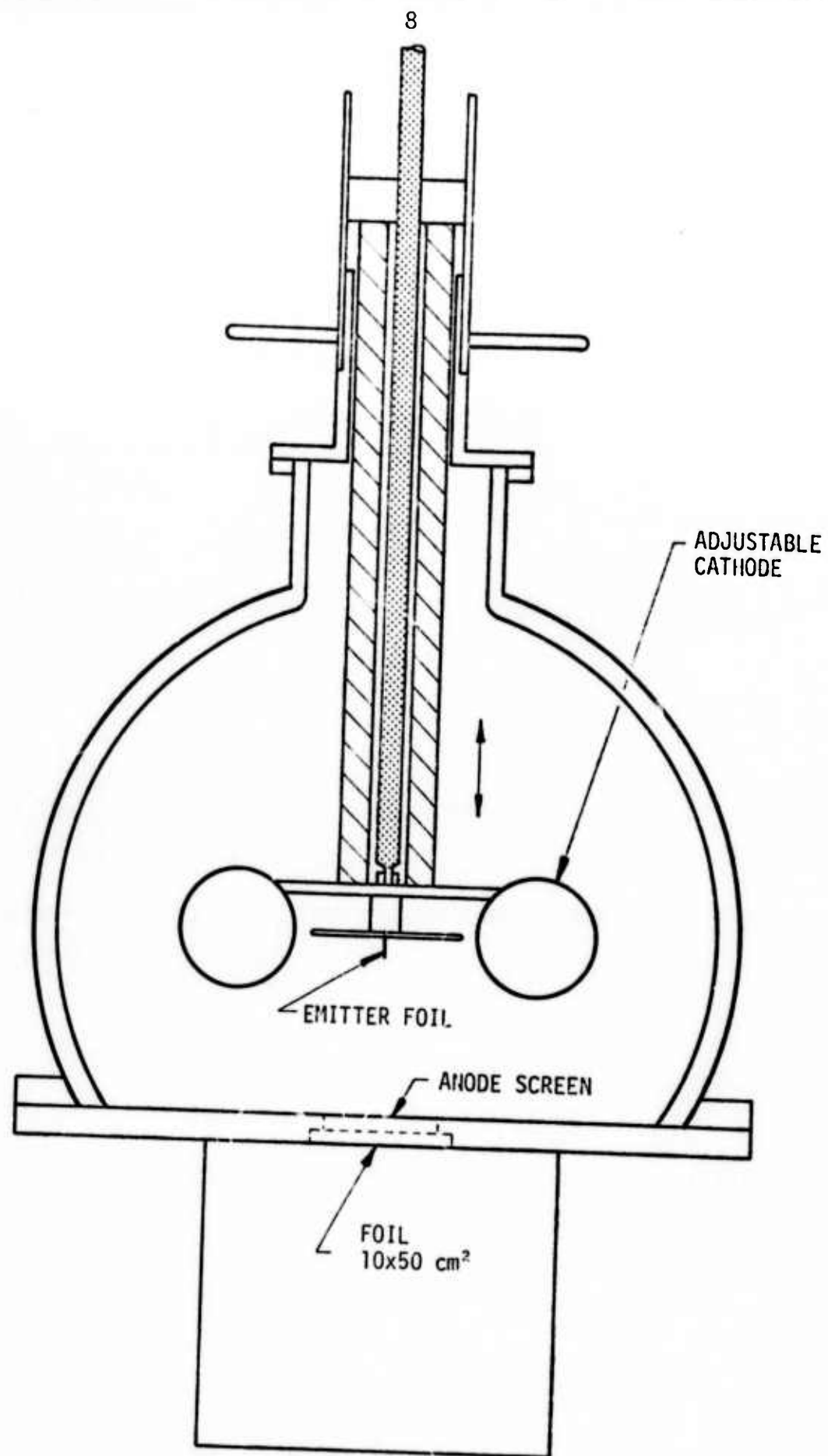Gun Showing the Toroidal Structure of the Cathode
which Provides Electrostatic Focusing of the e-Beam

CATHODE
VOLTAGE
90 kV/div

CURRENT
THROUGH FOIL
0.2 A/cm²/div

5 µsec

CATHODE TO ANODE
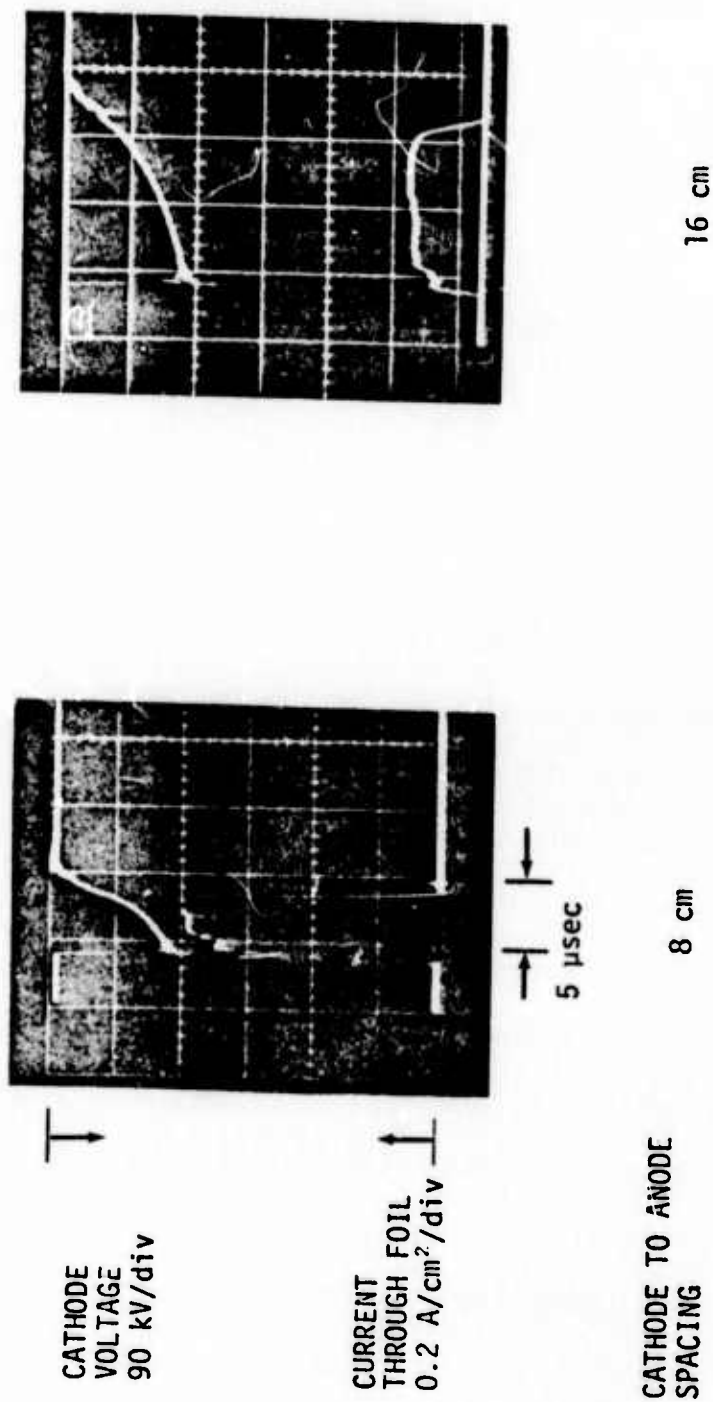SPACING

8 cm

16 cm

Figure 3. Oscilloscope Traces Showing the Electron Beam Current through the Foil as a
Function of Cathode to Anode Spacing for the Cold Cathode Electron Gun

2.3.1. Cl_2 Monitor

The chlorine molecule has an intense absorption band at 3300 Å with a long wavelength tail extending out to 4400 Å. Using the 3650 Å mercury line and narrow band transmittance filters, the Cl_2 concentration can be measured since the absorption coefficient versus wavelength is known (Ref. 5). The appropriate lenses for creating a collimated light beam from a small mercury lamp and the necessary filters have all been ordered. An experiment is planned to study the Cl_2 consumption rate in the plasma diode apparatus as a means for checking out the sensitivity of the monitoring technique. Following these tests, the chlorine monitor will be used in conjunction with HCl laser tests in the new high current cold cathode electron gun facility.

2.3.2. $H_2(v)$ Population by Coherent Raman Anti-Stokes Scattering

The excited $H_2(v)$ populations will be measured using coherent Raman anti-Stokes scattering, which provides many orders of magnitude more sensitivity than conventional Raman scattering. This technique has recently been applied by Regnier and Taran (Ref. 6) to measure small (10 - 100 ppm) H_2 concentrations in flames. The method is based on parametric four wave mixing: two collinear light beams of frequencies ω_1 and ω_2 generate a collinear (anti-Stokes) wave at frequency $2\omega_1 - \omega_2$ when traversing a gas containing a Raman active molecular species with vibrational frequency $\omega_{v,v+1} = \omega_1 - \omega_2$. The intensity of the generated wave is proportional to the square of the number density difference of the v and v + 1 vibrational levels and to $(I_1^2)(I_2)$, where

I_1 is the intensity of ω_1 and I_2 the intensity of ω_2. Focusing the source beams into the sample gas yields the largest anti-Stokes signal; however, the power collected is essentially independent of the f number of the optical system.

A tunable dye laser will be used to generate the $\omega_2 = \omega_1 - \omega_{v,v+1}$ frequency, and ω_1 will be the ruby laser line at 6943 Å. In order to study the excited H_2 vibrational levels, dyes capable of emitting at 9,800 Å to 9,000 Å are needed. Polymethine dye solutions discussed by Miyazoe and Maeda (Ref. 7) can provide laser output at these wavelengths using a ruby pumping laser. A monochromator or appropriate filters will be used to separate the incident laser wavelengths from the anti-Stokes signals.

Figure 4 shows a schematic of the optical arrangement which will be used. An H_2 reference cell will eventually be added to monitor the incident beam intensities which will correct for any non-reproducibility problems encountered in the ruby and dye lasers. The frequency of the dye laser will be adjusted using a monochromator to determine the absolute wavelength to within 1 Å.

The coherent Raman anti-stokes scattering signals which will be detected are proportional to the square of the population difference of levels v and v + 1. For example, if 10 percent of the H_2 molecules are excited to v = 1, the anti-Stokes signal will be reduced to 64 percent of the signal observed from an unexcited sample. If several H_2 levels are excited, the highest level occupied to any significant extent will be found and hence the differences measured for the lower levels can be reduced to absolute populations. For example, if it is
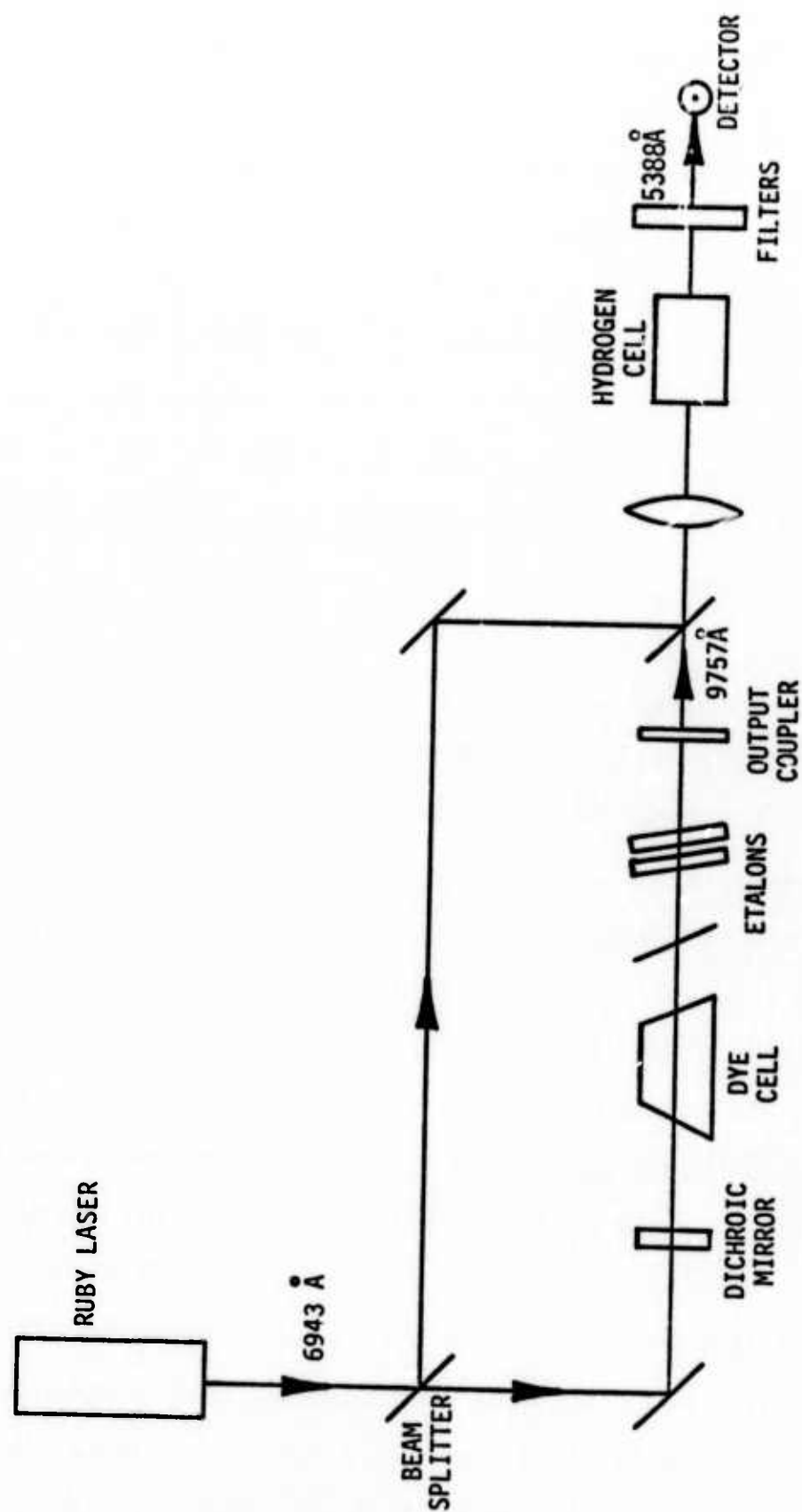
Figure 4. Coherent Anti-Stokes Raman Emission by Four-Wave Mixing in Hydrogen

found that the signal for the 4-3 population difference is insignificantly small compared to that found for 3-2, it is concluded that level 2 is the highest level with any significant population. Then by using the measured anti-Stokes signals observed for 0-1 and 1-2, combined with the known total H_2 concentration, the vibrational populations of the v = 0, 1, and 2 levels are readily calculable.

The signal intensities for the $H_2(v = 1)$ - $H_2(v = 2)$ transition calculated for different incident ruby and dye laser intensities are shown in Table II. $H_2(v)$ populations as low as 10^{-3} - 10^{-5} torr should be readily observable with conventional photomultiplier tubes and reasonable laser intensities.

Prior to attempting the hydrogen Raman experiments an experiment in liquid benzene will be tried. The optical arrangement for this experiment is shown in Figure 5. The purpose of this preliminary experiment is to gain familiarity with the lasing properties of the polymethine dyes and their tunability. Benzene presents a far less difficult case than H_2 due to the high molecular densities of a liquid (10^{21} molecules/cc) compared to a gas (10^{19} molecules/cc at 1 atmosphere) and the broader Raman linewidth of liquid benzene. These parameters would make the dye laser linewidth and output power less critical and allow one to gain familiarity with the technique. The proposed optical layout for the H_2 experiment (Figure 4) involves the use of two etalons to accomplish the tunability and line narrowing required. These components are still under study to determine whether a convenient set of etalons can be found and specifications for their purchase are being written.

TABLE II

COMPUTED COHERENT ANTI-STOKES SCATTERED
INTENSITY FROM $H_2(v=1)$

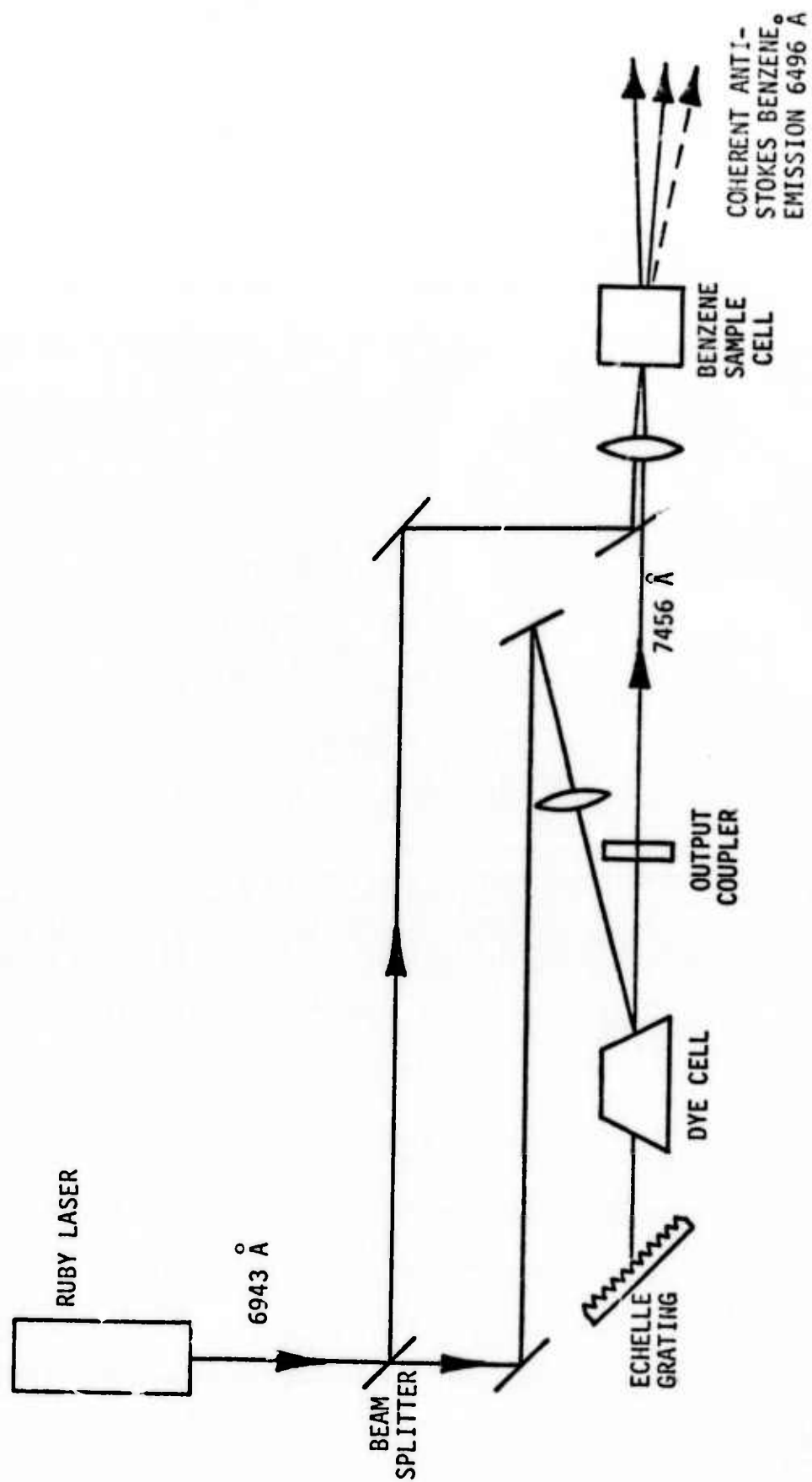| $H_2(v = 1)$ (torr)	Incident Laser Beams		Observed Anti-Stokes Signal Power (W)
	Laser Power (MW)	Stokes Power (MW)	
0.08	1	1	1
4×10^{-3}	20	1	1
8×10^{-3}	1	1	10^{-2}
4×10^{-4}	20	1	10^{-2}
8×10^{-4}	1	1	10^{-4}
4×10^{-5}	20	1	10^{-4}
8×10^{-3}	1	0.1	10^{-3}

Figure 5. Coherent Anti-Stokes Raman Emission by Four-Wave Mixing in Benzene

2.3.3. HCl Monitor

An HCl probe laser will be used to measure the HCl concentration in the test gas mixtures. A chemical HCl laser operating on the HCl vibrational-rotational levels has been described by Chang and Wood (Ref. 8) using a conventional pin laser and a similar apparatus will be used in this work. MSNW has successfully used this approach to measure HF and DF concentrations in a study of electrically excited HF and DF lasers (Ref. 4). The pin laser apparatus is currently being modified to allow operation with chlorine.

The problem of pressure induced line shift in the HCl measurements, in contrast to the HF system, will be eliminated by operating both the pin laser and test gas mixtures at the same total pressure and buffer gas concentration whenever possible. When different gas mixtures must be used, the system will be calibrated by measuring the absorption for gas mixtures containing known quantities of HCl.

The probe laser will also be used to measure HCl produced by pre-reaction in the sample gas mixtures as well as the HCl impurity level in the Cl_2 gas supply. HCl present in the initial gas mixtures could be detrimental to optimum laser performance.

2.4. Computer Model

A complete molecular kinetics model is being assembled based on the currently available experimental and theoretical rate constants. Recent theoretical calculations by R. Wilkins (Ref. 2) for the $Cl + HCl(v)$ deactivation rate are in excellent agreement with the experimental measurements of Moore, et al. (Ref. 3). Hence, Wilkins'

calculated values for the Cl + HCl(v) and H + HCl(v) deactivation rates (Ref. 2) and the Cl + H_2(v) reaction rate (Ref. 1) will be taken as good starting values for the HCl chemical reaction code. The code development will also make extensive use of a recent review by Cohen and Bott (Ref. 9) of the rate coefficients in the H_2 - Cl_2 chemical laser system. A reaction rate sensitivity study will be made to establish the importance of various unknown rate constants.

The Boltzmann electron transport equation for H_2/Cl_2/diluent mixtures will be solved based on currently available information on Cl_2, H_2, and HCl elastic, vibrational, and electronic excitation cross sections. The effect of superelastic electron collisions on H_2 and HCl will be investigated further as this may be a contributing deactivation mechanism for the vibrational levels.

SECTION III

CONCLUSIONS

Initial laser measurements during the first phase of the contract period have produced encouraging results on the performance of an electrically initiated HCl chemical laser. During the remainder of the present contract further laser performance measurements will be made in a new high current electron beam stabilized discharge apparatus. Diagnostics for measuring the Cl_2 concentration and $HCl(v)$ populations will be completed and some preliminary measurements will be made. A coherent Raman technique for measuring $H_2(v)$ will be tested and calibrated for use in discharge experiments. A computer code will be assembled and tested for modelling the HCl chemical reaction kinetics using the data available in the literature. Results of the computer model will then be compared to measurements of the HCl laser performance.

REFERENCES

1. R. L. Wilkins, Reaction Rates and Energy Distributions Among Reaction Products for the H + Cl_2 and Cl + H_2 Reactions, Report SAMSO-TR-75-53, Aerospace Corporation, February 21, 1975.

2. R. L. Wilkins, Vibrational Relaxation of HCl (v = 1, 2, 3, 6) by H and Cl Atoms, Reports SAMCO-TR-75-74, Aerospace Corporation, February 25, 1975.

3. R. G. Macdonald, C. B. Moore, I. W. M. Smith and F. J. Wodarczyk, J. Chem. Phys. 62, 2934 (1975).

4. S. R. Byron et al., Molecular Lasers in E-Beam Stabilized Discharges, MSNW Report No. 75-105-4, February, 1975.

5. J. G. Calvert and J. N. Pitts, Jr., Photochemistry, John Wiley and Sons, Inc., New York, 1966, p. 184, 198.

6. P. R. Regnier and J. P.-E. Taran, Appl. Phys. Lett. 23, 240 (1973).

7. Y. Miyazoe and M. Maeda, Appl. Phys. Lett. 14, 206 (1968).

8. O. R. Wood and T. Y. Chang, Appl. Phys. Lett. 20, 77 (1972).

9. N. Cohen and J. F. Bott, A Review of Rate Coefficients in the H_2-Cl_2 Chemical Laser System, Report SAMSO-TR-75-82, Aerospace Corporation, March 19, 1975.